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Heat Transfer Fluids for Low Temperature Application comprising Aromatic Hydrocarbons.

5 This invention relates to heat transfer fluids which can  
beneficially be used over a broad range of temperatures such as  
at temperatures from below  $-125^{\circ}\text{C}$  up to  $+175^{\circ}\text{C}$ . The inventive  
compositions consist essentially of a combination of, at least,  
two structurally non-identical aromatic components selected  
10 from the group consisting of polyalkyl-benzene and alkyl-  
benzene wherein the alkyl moiety is represented by branched or  
straight carbon chains having from 1 to 6 carbon atoms provided  
that the total number of carbon atoms in the alkyl moiety(ies)  
is in the range of from 1 to 10 or mixtures of such an aromatic  
15 component and an aliphatic hydrocarbon having a linear or  
branched chain with from 5 to 15 carbon atoms or mixtures  
thereof. The compositions are formulated to possess: a cloud  
point below  $-100^{\circ}\text{C}$ , preferably in the range of from  $-110^{\circ}\text{C}$  to  
 $-175^{\circ}\text{C}$ ; a vapor pressure at  $+175^{\circ}\text{C}$ , below 827 kPa; and a  
20 viscosity, measured at the cloud point temperature of the fluid  
 $+10^{\circ}\text{C}$ , below 400 cP.

Transfer fluids, in particular heat transfer fluids, have been  
used commercially for a long time. As one would consequently  
25 expect, the prior art relating to this domain is crowded and  
diverse and possessed of multiple improvement proposals, in  
particular with respect to improving the efficacy of such  
fluids at low temperatures. Presently, commercial heat transfer  
fluids can be used at temperatures down to  $-80^{\circ}\text{C}$ . Below that  
30 temperature, viscosity can be too high and/or products can be  
converted into solids. Several commercial products were

formulated to mitigate the negatives but were found to be unsuitable for application over a broad range of temperatures because of significant negatives including too high vapor pressures, too low flash points and/or too high viscosities at the operating temperatures. One of such commercial executions, which is based on methylcyclopentane, shows significant negatives, low flash point (-25 °C) and high vapor pressure which can render its utilization aleatory. A commercial silicon-based product has too high viscosity and freezing point and is, in addition, economically less attractive.

US-A-6,086,782 discloses heat transfer fluid compositions containing major, possibly comparable, levels of a terpene and an alkylbenzene. These compositions are said to retain the liquid state at any temperature in the range of from -18 °C to -115 °C. US-A-5,484,547 describes low temperature heat transfer fluids consisting of major levels of a glycol component and a second component selected from dioxolanes, glycol formal and dioxanes and minor levels of conventional additives. FR-A-1.427.017 relates to refrigerant fluids containing a mixed isopropyl/isobutyl orthosilicate tetraester and a minor level of an ethyl/butyl propyleneglycol diether. These compositions can be used at temperatures down to -54 °C. Phillip E. Tuma, Pharmaceutical Technology, March 2000, pages 104-114, has summarized various obstacles on the road to achieving beneficial low temperature heat transfer performance. Particular attention is drawn, among others, to flammability, environmental effects and thermal performance. EP-A-92 089 922.1 pertains to working fluids comprising a mixture of fluoroalkanes and hydrofluoroalkanes, possibly in equal weight proportions. The compositions can be used in refrigerators,

freezers, heat pumps and air conditioning systems.

Hydrofluorocarbons do not meet the requirements of this invention among others because of excessive vapor pressures at temperatures above e.g. 100 °C. While known fluids could be  
5 used at selected low temperature conditions, such known fluids are generally inadequate, in particular for use at higher temperatures.

The negatives attached to prior art low-temperature fluids are  
10 operationally significant; the actual application of the art technology is capital intensive and cannot yield manufacturing flexibility over a broad range of temperatures.

It is therefore a major object of this invention to provide  
15 heat transfer fluids capable of operating over a broad range of temperatures. It is another object of this invention to formulate heat transfer fluids capable of being used effectively at a broad range of temperatures, particularly from -125 °C to +175 °C while avoiding significant vapor pressure  
20 build-up and maintaining adequate fluidity properties. It is yet another object of this invention to formulate heat transfer fluids having acceptable physical properties. The foregoing and other benefits can now be secured from heat transfer fluids comprising a mixture of, at least, two structurally non-  
25 identical alkyl- and/or polyalkyl-benzenes, or a mixture of an aromatic alkyl- and/or polyalkyl-benzene component and an aliphatic hydrocarbon, or mixtures thereof. The levels of the individual components in a fluid composition of this invention are selected such that the composition exhibits cumulative  
30 physical properties, including a cloud point below -100 °C, a vapor pressure at +175 °C below 827 kPa, and a viscosity,

measured at the cloud point temperature  $+10^{\circ}\text{C}$ , below 400 cP. The inventive technology herein is described in more detail hereinafter.

- 5 Particular terms as used throughout the description and the claims shall have the following meaning:

"cloud point" is defined as the temperature of equilibrium between a multicomponent liquid of specified composition and  
10 the first solid phase that appears when that liquid is cooled, measured in accordance with the method of ASTM D-2500. The cloud point of the liquid heat transfer fluid can also be calculated in accordance with the method of S.I. SANDERS, Chemical and Engineering Thermodynamics, Wiley, New York, 1977,  
15 Chapter 8;

"vapor pressure" is measured thereby using the method of PROCESS HEATING, November/December 1994, page 27, Volume 1, Number 4, or calculated by methods described in R.C. REID, J.M.  
20 PRAUSNITZ and T.K. SHERWOOD, The Properties of Gases and Liquids, McGraw-Hill, New York, 1977;

"viscosity" is determined in accordance with the method of ASTM D-445, or calculated by the method of VAN VELZEN, CARDOZO and  
25 LANGENKAMP as described in R.C. REID, J.M. PRAUSNITZ and T.K. SHERWOOD, The Properties of Gases and Liquids, McGraw-Hill, New York, 1977, Chapter 9;

the term "alkyl" embraces, unless defined differently, straight  
30 or branched species;

the term "aliphatic hydrocarbon" is/can be used interchangeably with the term "aliphatic alkane";

5 "percent" or "%" refers, unless defined more specifically, to percent or % by weight; and

the term "structurally non-identical" means that the first aromatic component has a different molecular weight as compared to the second aromatic component or that the first and the  
10 second aromatic components are structural isomers.

This invention concerns heat transfer fluids which can be used beneficially over a broad range of temperatures such as at temperatures from below -125 °C up to +175 °C. The heat  
15 transfer fluid compositions herein consist essentially of (a) a mixture of at least two structurally non-identical components selected from the group consisting of alkyl-benzene and polyalkyl-benzene wherein the alkyl moiety is represented by branched or straight carbon chains having from 1 to 6 carbon  
20 atoms provided that the total number of carbon atoms in the alkyl moiety(ies) is in the range of from 1 to 10; and (b) a mixture of an aromatic component selected from the group consisting of alkyl-benzene and polyalkyl benzene wherein the alkyl moiety is represented by branched or straight carbon  
25 chains having from 1 to 6 carbon atoms provided that the total number of carbon atoms in the alkyl moiety(ies) is in the range of from 1 to 10 and an aliphatic hydrocarbon having a linear or branched chain with from 5 to 15 carbon atoms or mixtures thereof, at a level such that the composition has a cloud point  
30 below -100 °C, preferably in the range of from -110 °C to -175 °C, a vapor pressure, at +175 °C, below 827 kPa, and a

viscosity, measured at the cloud point temperature +10 °C, below 400 cP.

In preferred executions herein, the aliphatic hydrocarbon  
5 contains from 5 to 10 carbon atoms, the viscosity is below 300 cP and the vapor pressure, at +175 °C, is below 621 kPa.

The heat transfer fluids of this invention consist essentially of a mixture of at least two structurally non-identical  
10 aromatic components selected from alkyl-benzene and polyalkyl-benzene. The two structurally non-identical aromatic components are either distinguished by different molecular weights and thus translate, for example, into a different number of carbon atoms and/or a different number of hydrogen atoms in such  
15 aromatic components. Such non-identical aromatics can also be represented by structural isomers. Examples of structurally non-identical isomers are: ortho- and meta-xylene; and n-propylbenzene and iso-propylbenzene. Examples of non-identical aromatic components having the same number of carbon atoms and  
20 a different number of hydrogen atoms are n-butylbenzene and tetrahydronaphthalene. The ponderal ratios of the structurally non-identical aromatic components are generally within the range of from 1st component: 2nd component of from 95 : 5 to 5 : 95, preferably in the range of from 80 : 20 to 20 : 80. The  
25 alkyl moiety in the aromatic component is preferably represented by any one of the following species: methyl; ethyl; dimethyl; ethylmethyl; trimethyl; n-propyl; n-butyl; methyl(n-propyl); di-ethyl; tetramethyl; n-pentyl; ethyl(n-propyl); methyl(n-butyl); n-hexyl; di(n-propyl); tri-ethyl or mixtures  
30 thereof.

Examples of individually preferred aromatic components are toluene, n-propylbenzene, ethylbenzene and n-butylbenzene. The aromatic species can be used in preferred combinations of structurally non-identical species (with or without aliphatic hydrocarbons) such as, at least, binary combinations of:

5 toluene/ethylbenzene; toluene/n-propylbenzene; ethylbenzene/n-butylbenzene; n-propylbenzene/n-butylbenzene; ethylbenzene/n-propylbenzene; and toluene/n-butylbenzene. Examples of suitable ternary combinations of non-identical aromatic components, with

10 or without aliphatic hydrocarbons, are: n-propylbenzene/toluene/ethylbenzene; ethylbenzene/n-propylbenzene/n-butylbenzene; n-propylbenzene/n-butylbenzene/toluene and ethylbenzene/toluene/n-butylbenzene. The ponderal ratios of aromatic/alkane combinations are

15 frequently in the range of from 10 : 90 to 90 : 10, preferably of from 15 : 85 to 80 : 20, and more preferably of from 20 : 80 to 70 : 30.

The essential aliphatic alkane (aliphatic hydrocarbon)

20 component has a linear or branched chain with from 5 to 15, preferably from 5 to 10 carbon atoms.

Representative and preferred species of the aliphatic alkanes are: pentane-2,2,4-trimethyl; pentane-2,3,4-trimethyl; pentane-

25 2-methyl; pentane-3-methyl; hexane-2-methyl; hexane-3-methyl; n-hexane; hexane-2,2-dimethyl; hexane-3,3-dimethyl; n-heptane; heptane-4-methyl; n-octane; and octane-2-methyl. The aliphatic alkane component can be represented by the individual species or by a mixture of species.

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The inventive compositions herein can contain, as optional

components, additive levels, generally less than 8 %, preferably less than 5 %, expressed in reference to the essential components (100 %) of the heat transfer fluid composition, of fully hydrogenated hydrocarbons corresponding  
5 to the essential aromatic component in accordance with the claims. The use of unsaturated hydrocarbons, such as terpenes and unsaturated derivatives and/or analogues thereof can adversely affect the performance of the claimed fluids and shall therefore also be limited to levels below 8 %, preferably  
10 below 5 % expressed in reference to the essential components (100 %) of the claimed heat transfer fluid.

The inventive compositions can in addition contain, as optional components, additive levels of ingredients that can serve for  
15 optimizing and enhancing performance of the inventive compositions. The like additives are well-known in the domain of heat transfer fluids and are generally used in art-established levels. Specific examples of suitable additives include anti-oxidants, dyes and acid scavengers. The term  
20 "additive level" is meant to define a cumulative level of from 0.01 % to 4 %, preferably from 0.01 % to 2 %

Performance parameters of a series of examples in accordance with this invention were determined thereby using the methods  
25 recited in the patent description. The results are listed in the following tables whereby the column headings refer to the following:

A = Sample Number;

30

B = Cloud Point in °C;



C = Vapor Pressure at +175 °C in kPa; and

D = Viscosity in cP at cloud point temperature + 10 °C.

5

E = Ponderal (weight %) Fraction of Components.

	A	B	C	D	E	COMPONENTS
10						
	8	-129.7	561.9	37.5	41.8	2-Methylhexane
					30.4	n-Propylbenzene
					27.8	Toluene
15	9	-128.6	309.5	60	36.6	n-Propylbenzene
					28.3	Ethylbenzene
					35.1	Toluene
20	10	-128.5	617	30.4	47.5	2-Methylhexane
					23.6	Ethylbenzene
					28.9	Toluene
25	11	-127.7	524.6	32	48.7	2-Methylhexane
					30.4	n-Propylbenzene
					20.9	Ethylbenzene
30	12	-127.5	784	21	63.6	2-Methylhexane
					13.4	n-Hexane
					23.0	Toluene

	13	-127	700.5	22	61.8 24.7 13.5	2-Methylhexane n-Propylbenzene n-Hexane
5	14	-126.8	624	28	54.7 27 18.3	2-Methylhexane Toluene n-Butylbenzene
10	15	-126.3	703.2	23	66.2 20.6 13.2	2-Methylhexane Toluene n-Heptane
15	16	-126.1	537.8	29.5	59.9 26.5 13.6	2-Methylhexane n-Propylbenzene n-Butylbenzene
	17	-125.3	279.2	62	40.2 36.7 23.1	n-Propylbenzene Toluene n-Butylbenzene
20	18	-125	580.5	25	61.3 21.0 17.7	2-Methylhexane Ethylbenzene n-Butylbenzene
25	19	-124	320.6	45.6	34.3 40.2 25.5	Ethylbenzene Toluene n-Butylbenzene
30	19	-123.7	713.6	20	74.6 25.4	2-Methylhexane Toluene
	20	-123.3	608.1	21.5	71.4	2-Methylhexane

					28.6	n-Propylbenzene
	21	-123.1	716.4	24	27.1	2-Methylpentane
					42.5	n-Propylbenzene
5					30.4	Ethylbenzene
	22	-122.7	433	43.3	17.1	2,2,4-Trimethylpentane
					45.0	n-Propylbenzene
					37.9	Toluene
10						
	23	-122.1	173.7	58.1	42.7	n-Propylbenzene
					32.3	Ethylbenzene
					25.0	n-Butylbenzene
15	24	-121.8	441.9	31.6	48.9	n-Propylbenzene
					8.3	n-Hexane
					42.8	Toluene
	25	-121.7	370.9	39.3	49.3	n-Propylbenzene
20					42.1	Toluene
					8.6	n-Heptane
	26	-121.3	505.4	32	22.5	2,2,4-Trimethylpentane
					36.6	Ethylbenzene
25					40.9	Toluene
	27	-121.1	541.2	22.8	11.6	n-Hexane
					41.7	Ethylbenzene
					46.7	Toluene
30						
	28	-120.6	375	39.5	27.1	2,2,4-Trimethylpentane

					42.2	n-Propylbenzene
					30.7	Ethylbenzene
5	29	-120.3	651.5	20.5	53.6	2,2,4-Trimethylpentane
					26.6	n-Propylbenzene
					19.8	n-Hexane
10	29	-120.0	427.5	28.2	42.1	Ethylbenzene
					47.7	Toluene
					10.2	n-Heptane
15	30	-119	319.2	38.2	53.6	n-Propylbenzene
					46.4	Toluene
	31	-118.8	275.1	35.6	51.4	n-Propylbenzene
					37.9	Ethylbenzene
					10.7	n-Heptane
20	32	-118.5	513.6	32.2	38.6	2,2,4-Trimethylpentane
					34.5	Toluene
					26.9	n-Butylbenzene
25	33	-118.2	324.7	29	45.4	n-Propylbenzene
					40.3	n-Hexane
					14.3	Ethylbenzene
	34	-117.5	560	20.3	15.9	n-Hexane
					47.5	Toluene
30					36.6	n-Butylbenzene
	35	-117.2	376.5	26.3	47.5	Ethylbenzene
					52.5	Toluene

5	36	-116.9	403.3	24.7	51.5	n-Propylbenzene
					16.3	n-Hexane
					32.2	n-Butylbenzene
10	37	-116.6	440.6	29.6	47.3	2,2,4-trimethylpentane
					28.4	Ethylbenzene
					24.3	n-Butylbenzene
15	38	-116.0	407.5	28.3	48.7	Toluene
					13.3	n-Heptane
					38.0	n-Butylbenzene
20	39	-115.8	200.6	35.7	57.1	n-Propylbenzene
					42.9	Ethylbenzene
	40	-115.5	230.3	39.1	52.7	n-Propylbenzene
25					25.4	n-Heptane
					21.9	n-Butylbenzene
	41	-115.1	481.9	18.1	18.8	n-Hexane
30					43.4	Ethylbenzene
					37.8	n-Butylbenzene
	42	-115.0	602.6	14.4	53.6	n-Propylbenzene
					24.5	n-Hexane
					21.9	n-Heptane

	43	-113.7	296.5	26.6	45.5	Ethylbenzene
					15.8	n-Heptane
					38.7	n-Butylbenzene
5	44	-113.7	478.5	24.4	67.9	2,2,4-Trimethylpentane
					32.1	n-Propylbenzene
	45	-113.6	622.6	20.6	75.2	2,2,4-Trimethylpentane
					24.8	Toluene
10	46	-113.2	711.5	10.7	32.7	n-Hexane
					39.0	Toluene
					28.3	n-Heptane
15	47	-111.9	331	27.7	55.0	Toluene
					45.0	n-Butylbenzene
	48	-111.6	125	45.6	60.4	n-Propylbenzene
					39.6	n-Butylbenzene
20	49	-111.2	712.2	10.3	34.0	n-Hexane
					29.9	n-Heptane
					36.1	n-Butylbenzene

25 The foregoing testing results illustrate the superior performance of the inventive technology.

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